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(54) PROCESS FOR PRODUCING PULLULAN FIBRES

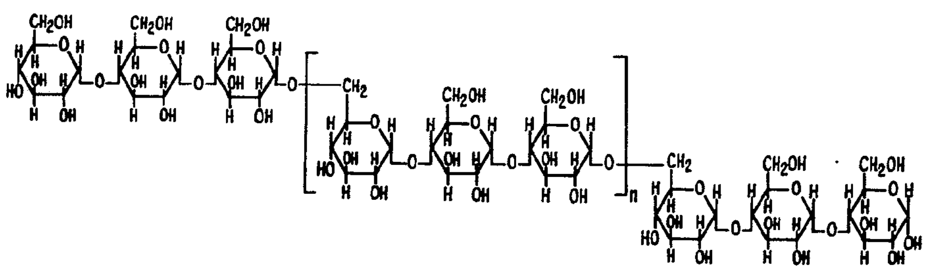
(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a Corporation of Japan of 15, Kitahama-5-Chome, Higashi-ku, Osaka, Japan and HAYASHIBARA BIOCHEMICAL LABORATORIES, INC., a Corporation of Japan of 2—3, Shimoishii-1-Chome, Okayama-shi, Okayama-ken, Japan, respectively, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a novel fibre containing pullulan, which is a polymer having repetition units of maltotriose.

Pullulan decomposes at about 250°C when heated in an absolutely dry state, but does not melt at a temperature between room temperature and the thermal decomposition temperature thereof. Japanese Patent Laid-Open (Kokai) No. 21739/73 discloses a process in which pullulan is lowered in melting temperature by addition of water as a plasticizer, and it is possible to obtain a fibre by subjecting pullulan containing less than 25% of water to extrusion at a temperature of 110° to 120°C under a pressure of 100 to 150 kg/cm².

The present invention provides a process for producing a pullulan-containing fibre, which comprises using as a spinning solution an aqueous solution of pullulan or a melt of pullulan plasticized with water, and extruding the spinning solution at a temperature up to 100°C through a nozzle into a gas phase.

The pullulan referred to in the present invention is a linear high polymer in which units of maltotriose, which is a trimer of glucose, are repeatedly bonded through 1,6-linkages, and has the molecular structure represented by the formula,



wherein n is an integer of 20 to 10,000 which shows the polymerization degree, and various modified pullulans may also be used as hereinafter described.

Heretofore, pullulan has not been used in the commercial fibre industry.

While the pullulan used in the present invention contains glucose units in its molecule, it is entirely different in molecular structure, and greatly different in properties from starch, oxidised starch, enzyme degraded starch, etherized starch, cationized starch, animated starch, cellulose, alkyl cellulose, hydroxyalkyl cellulose, carboxymethyl cellulose, and gum arabic which are conventional glucose derivatives composed mainly of glucose units.

The aqueous solution containing pullulan or the melt of pullulan plasticized with water is adjusted to a temperature of up to 100°C, preferably 70° to 20°C, more preferably 50° to 20°C, and is extruded through a nozzle into a gas phase.

The present inventors have found that pullulan can be easily spun at temperatures lower than those previously considered necessary, taking advantage of the facts that pullulan and cold water are homogeneously miscible with each other in all proportions, that an aqueous solution of pullulan is high in fibre-forming ability, and that an aqueous pullulan solution is stable over a long period of time.

Pullulan has excellent water solubility, its solubility in cold water being higher than that of other water-soluble polymer. For example, a conventional water-soluble polymer, polyvinyl alcohol, is scarcely soluble in cold water, though the extent of water solubility varies depending on the saponification degree of the polyvinyl alcohol, and it is usual to prepare aqueous polyvinyl solutions by spraying steam at above 110°C into the system to dissolve the polyvinyl alcohol. Another such polymer, carboxymethyl cellulose, has the disadvantage that when charged into water at one time, it forms undissolved lumps, making it difficult to obtain a homogeneous aqueous solution. Further, the viscosity of an aqueous solution of pullulan is far lower than that of a comparable aqueous solution of carboxymethyl cellulose or polyvinyl alcohol. This low viscosity, coupled with the specific water solubility of pullulan, has made it possible that the aqueous pullulan solution, when used as a spinning solution at the low temperatures specified above, is easily spun into filaments by extrusion through a nozzle into air, nitrogen or other gas.

The pullulan used in the present invention can homogeneously absorb various amounts of water either in the form of steam or by water spraying or similar procedure, and does not require any preliminary heating operation for homogeneous solution in water. Being non-crystalline and hence easy to handle, pullulan has marked advantages in the production of pullulan fibres, not least in that an aqueous pullulan solution is stable over a long period of time at any concentration, and does not undergo gelation or so-called "aging" phenomena as observed in aqueous starch solutions.

It is an advantage of pullulan that the aqueous pullulan solution or pullulan melt is low in viscosity at relatively low temperatures and hence can be extruded at a relatively low extrusion pressure. The spinnability of an aqueous pullulan solution or melt at the aforesaid relatively low temperatures is not only advantageous from the standpoint of thermal efficiency, but also has the great practical advantage that the temperature control and uniformity of temperature distribution can be facilitated to make the spun filaments uniform in quality.

The tensile strength of starch fibres produced according to a known process is about 300 kg/cm^2, whereas that of the pullulan fibre produced according to the process of the present invention is 2,520 kg/cm^2 and thus is more than 8 times the strength of said starch fibre (refer to Example 1 hereinafter).

The water content of the pullulan spinning solution used in the present invention is desirably in the range of 5 to 99 wt%, preferably 30 to 80 wt% and spun filaments can be obtained by properly balancing the temperature of the spinning solution with the molecular weight of the pullulan, the shape and size of the spinning nozzle, and the extrusion pressure. For example, when a spinning solution of pullulan having a molecular weight of 150,000 is extruded through a cylindrical nozzle of 0.3 mm in diameter and 1 mm in length at room temperature under a pressure of 1 to 10 kg/cm^2, the water content of the pullulan spinning solution is desirably in the range of 30 to 80 wt%, preferably 50 to 70 wt%.

The pullulan may incorporate, in addition to water, as a plasticizer or softener, a polyhydric alcohol such as glycerin, sorbitol, maltitol, ethylene glycol, propylene glycol, polyethylene glycol or polypropylene glycol, or dimethyl sulphoxide.

If necessary, the spinning solution may be subjected, in order to improve the physical properties of the spun filaments and fabrics obtained therefrom, to mixed-spinning in admixture with other water-soluble polymers such as polyvinyl alcohol, polyethyleneimine, polyacrylamide, polyacrylic acid, sodium polyacrylate, polyvinyl pyrrolidone, polyethylene oxide, sodium alginate, carboxymethyl cellulose or hydroxyethyl cellulose, or an emulsion of a water-insoluble polymer such as polyvinyl acetate, polyethyl acrylate, polypropyl acrylate, poly n-butyl acrylate, polymethacrylic acid, polymethyl methacrylate, polypropyl methacrylate, polybutyl methacrylate, polystyrene, polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile or ethylenevinyl acetate copolymer.

Further, the spinning solution may incorporate inorganic and organic additives which include colorants such as pigments and dyes; antioxidants such as phenyl-α-naphthylamine, phenyl-β-naphthylamine, N,N′-diphenyl-p-phenylenediamine, N,N′-di-β-naphthyl-p-phenylenediamine, N,N′ - diaryl - p - phenylenediamine, N - isopropyl - N′ - phenyl - p - phenylenediamine, aldol - α - naphthylamine, 6 - ethoxy - 2,2,4 - trimethyl - 1,2 - dihydroquinoline, 1,1 - bis(4 - hydroxyphenyl)cyclohexane,

2,6 - di - tert - butyl - p - cresol, 2,2′ - methylene - bis - (4 - methyl - 6 - tert - butylphenyl), 4,4′ - thiobis - (6 - tert - butyl - 3 - methylphenol), syrenated phenol; ultraviolet light absorbers such as phenyl salicylate, p-octylphenylsalicylate, 4-tert-butylphenyl salicylate, 2,4-dihydroxybenzophenone, 2 - hydroxy - 4 - methoxybenzophenone, 2,2′ - dihydroxy - 4 - methoxybenzophenone, 2 - hydroxy - 4 - octoxybenzophenone, 2 - hydroxy - 4 - methoxy - 2′ - carboxybenzophenone, 2,2′ - dihydroxy - 4,4′ - dimethoxybenzophenone, resorcinol monobenzoate, 2 - (2′ - hydroxy - 5′ - methylphenyl)benzotriazole; fillers such as calcium carbonate, clay, activated calcium fluoride, dolomite, talc, alumina white, mica powder, aluminum sulfate and barium sulfate; and flame retardants such as antimony oxide, antimony silico oxide, tris-(β-chloroethyl)phosphate, tris(chloropropyl)phosphate, tris(dichloropropyl)phosphate, tris(2 - bromoethyl)phosphate, triphenylphosphite, tris(2 - chloroethyl)phosphite, chlorinated paraffin and tetrabromoethane.

Fibres spun according to the present invention may be stretched in steam at 60° to 120°C, whereby the fibres can be further enhanced in strength, Young's modulus and knot strength.

Simple pullulan fibres are useful in various fields, but are high in water solubility, so that it may be necessary to control the degree of water solubility or to insolubilize the pullulan fibres according to the practical requirements. For this purpose, the formed pullulan fibres can be insolubilized by crosslinking with crosslinking agents for hydroxy-group-containing compounds including aldehydes such as formaldehyde, acetaldehyde, n-butylaldehyde and glyoxal, various epoxy resins, diisocyanates, and methylol compounds such as dimethylol-urea and dimethylol ethylene urea. Alternatively, the pullulan fibres can be insolubilized by incorporating bichromates into the fibres and then crosslinking the fibres by irradiation with light.

It is also possible to insolubilize the pullulan fibres by previously incorporating into the pullulan spinning solution a mixture comprising a monofunctional monomer such as acrylamide, acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate or N-vinyl pyrrolidone, and a polyfunctional monomer such as ethylene glycol dimethacrylate, a polyethylene glycol dimethacrylate such as diethylene-, triethylene-, or nonaethylene-glycol dimethacrylate, or methylene-bis-acrylamide, and an initiator such as hydrogen peroxide, ammonium persulphate, potassium persulphate, cerium (IV) ammonium nitrate, cerium (IV) ammonium sulphate, azo-bis-isobutyronitrile, t-butylperoxide, di-t-butyl peroxide, dicumyl peroxide, cumene hydroperoxide and t-butyl hydroperoxide, spinning the resulting mixture to obtain pullulan fibres, and then crosslinking the fibres by application of heat, light or radiation. Further, in order properly to control the water solubility of the pullulan fibres, there may be used in the spinning solution a modified pullulan prepared by subjecting pullulan to esterification, alkyl etherification, hydroxyalkyl etherification, carboxyalkyl etherification, phosphatization, oxidation, reduction or graft-copolymerization with a vinyl monomer, within a range where the modified pullulan is water-soluble.

Characteristic features of a pullulan fibre obtained by the spinning process of the present invention are as follows:

(1) The fibre dissolves quite quickly not only in hot water but also in cold water.

(2) The strength and Young's modulus of a single fibre are such that the fibre can successfully be put into practical use even when it has not been stretched (refer to Examples 1 and 2 as hereinafter described).

(3) The surface of the fibre has a beautiful silk-like gloss.

(4) The fibre is colorless and transparent, and the surface and interior thereof are markedly excellent in dyeability.

(5) The fibre is hydrophilic and moisture-absorptive, so that it generates no static electricity and thus is antistatic.

(6) The fibre is edible, non-toxic, tasteless and odorless, and is non-irritative to the skin.

(7) Even when burned, the fibre does not generate any poisonous gases such as nitrogen oxides and hydrogen chloride. Further, the fibre, after use, can be discarded as it is, since it is biodegradable in water and soil, and thus does not cause any significant pollution problems.

The pullulan fibres can be made into paper by subjecting them to paper-making, either singly or in admixture with wood pulp, hemp or ramie fibres, using as a dispersant a hydrophilic low molecular weight alcohol such as methanol, ethanol or isopropanol, or a hydrophilic organic solvent such as acetone which does not dissolve pullulan. The thus obtained papers are quickly soluble in water and excellent in printability, and hence can be used as papers for secret documents. Further, they are edible and digestable, and hence can be used directly as inner packings for

medicines and as small bags for packing seasonings for convenience foodstuffs and for tea power, coffee, cocoa and similar foods. Furthermore, they are water-soluble and non-irritative to the skin, and hence can be used as women's sanitary towels, toilet papers and tissue papers.

Alternatively, the pullulan fibres can be used as binders for non-woven fabrics, taking advantage of their tackiness. When fibres obtained from pullulan which has partly been water-insolubilized, or formed pullulan fibres which have partly been water-insolubilized, are spun either singly or in admixture with other fibres, the resulting spun product can be used in underwear and other clothes, taking advantage of the moisture-absorptivity, antistatic property and dyeability of the fibres.

The pullulan used in the present invention can be produced by any convenient method. It can be isolated and recovered as a tacky substance secreted in a culture liquor of a strain belonging to the genus *Pullularia*. For example, a strain of the species *Pullularia pullulans* is cultured with shaking at 24°C for 5 days in a medium containing (by weight) 10% of partially hydrolyzed starch, 0.5% of K_2HPO_4, 0.1% of NaCl, 0.02% of $MgSO_4 \cdot 7H_2O$, 0.06% of $(NH_4)_2SO_4$ and 0.04% of yeast extract, whereby pullulan is obtained as a tacky substance secreted from the cells into the culture liquor. If desired, the cells are removed by centrifugation from the culture liquor, and the supernatant liquid is charged with methanol to deposit a pullulan precipitate. After repeated water dissolution and methanol precipitation, purified pullulan can be obtained. Pullulan varies somewhat in physical properties depending on the kind of strain used, but this does not greatly influence its use in fibres.

The molecular weight of the pullulan used in the present invention is not particularly critical, but is preferably in the range of 10,000 to 5,000,000.

The present invention is illustrated in detail below with reference to examples.

Example 1

Pullulan having a molecular weight of about 150,000 was dissolved in water to prepare a spinning solution containing 40 wt% of said pullulan. The spinning solution was extruded at room temperature (23°C) under a pressure of 2 kg/cm² through a cylindrical nozzle of 0.3 mm in diameter and 1 mm in length into air at room temperature. The strand from the nozzle was wound up by means of a winding machine, whereby spun filaments were obtained. The thus obtained filaments were about 20 microns in diameter, and the unstretched fibre had a tensile strength of 2,520 kg/cm², an elongation of 20% and a Young's modulus of 15,000 kg/cm². When dipped into water at room temperature, the fibre dissolved virtually instantaneously.

Example 2

A pullulan fibre spun under the same conditions as in Example 1 was stretched in steam at 90°C to three times the original length thereof. The thus stretched pullulan fibre had a tensile strength of 2,900 kg/cm², an elongation of 17%, and a Young's modulus of 28,000 kg/cm². When dipped into water at room temperature, the fibre dissolved instantaneously.

Example 3

Pullulan having a molecular weight of about 200,000 was adjusted to a water content of 30 wt% by spraying water thereto. The pullulan thus treated was extruded at 70°C under a pressure of 30 kg/cm² through a cylindrical nozzle of 0.5 mm in diameter and 1 mm in length into air at room temperature, and the resulting filaments were wound up. The filaments were about 30 microns in diameter, and the unstretched fibre had a tensile strength of 2,610 kg/cm², an elongation of 18%, and a Young's modulus of 16,500 kg/cm². When dipped into water at room temperature, the fibre dissolved instantaneously.

WHAT WE CLAIM IS:—

1. A process for producing a pullulan-containing fibre, which comprises using as a spinning solution an aqueous solution of pullulan or a melt of pullulan plasticized with water, and extruding the spinning solution at a temperature up to 100°C through a nozzle into a gas phase.

2. A process according to Claim 1, wherein the spinning solution contains 5 to 99 wt% of water.

3. A process according to Claim 1 or 2, wherein a plasticizer or a softener is incorporated in the spinning solution.

4. A process according to Claim 3, wherein the plasticizer or softener is glycerin,

sorbitol, maltitol, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol or dimethyl sulphoxide.

5. A process according to any one of the preceding claims, wherein the spinning solution is used in admixture with a water-soluble polymer or an emulsion of water-insoluble polymer.

6. A process according to Claim 5, wherein the water-soluble polymer is polyvinyl alcohol, polyethyleneimine, polyacrylamide, polyacrylic acid, sodium polyacrylate, polyvinyl pyrrolidone, polyethylene oxide, sodium alginate, carboxymethyl cellulose or hydroxyethyl cellulose.

7. A process according to Claim 5, wherein the water-insoluble polymer is polyvinyl acetate, polyethylacrylate, polypropylacrylate, poly-n-butylacrylate, polymethacrylic acid, polymethylmethacrylate, polypropylmethacrylate, polybutylmethacrylate, polystyrene, polyvinylchloride, polyvinylidenechloride, polyacrylonitrile or ethylene-vinylacetate copolymer.

8. A process according to any one of the preceding claims, wherein the spinning solution includes a colourant, and/or antioxidant and/or ultraviolet light absorber and/or filler and/or flame-retardant.

9. A process according to any one of the preceding claims, wherein the spinning solution includes a mono-functional monomer, a polyfunctional monomer and an initiator adapted to produce a water-insolubilised fibre by application of heat, light or radiation to the spun fibre.

10. A process according to Claim 9, wherein the monofunctional monomer is acrylamide, acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, or N-vinyl pyrrolidone.

11. A process according to Claim 9 or 10, wherein the polyfunctional monomer is ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, nonaethylene glycol dimethacrylate or methylene-bis-acrylamide.

12. A process according to Claim 9, 10 or 11, wherein the initiator is hydrogen peroxide, ammonium persulfate, potassium persulfate, cerium (IV) ammonium nitrate, cerium (IV) ammonium sulfate, azobis-isobutyronitrile, t-butylperoxide, di-t-butylperoxide, dicumylperoxide cumene hydroperoxide or t-butyl hydroperoxide.

13. A process according to any one of Claims 1—8 followed by the step of insolubilising the fibre by cross-linking with formaldehyde, acetaldehyde, n-butylaldehyde, glyoxal, epoxy resin, diisocyanate, dimethylolurea or dimethylolethyleneurea.

14. A process according to any one of Claims 1—8 followed by the step of insolubilising the fibre by treatment with a bichromate and irradiation with light.

15. A process according to any one of Claims 9—12, wherein said water-insolubilized fibre is produced by subjecting the fibre, after spinning, to heat, light or radiation.

16. A process according to any one of the preceding claims, wherein the fibre is stretched at a temperature of 60°—120°C.

17. A process according to Claim 1, substantially as hereinbefore described with reference to any one of the Examples.

18. A fibre obtained by a process according to any one of the preceding claims.

19. An insolubilised fibre obtained by a process according to any one of Claims **9—15.**

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